

Adsorption and Solution of Weakly Polar Vapors with Thin Layers of Water as Studied by Gas-Liquid Chromatography

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This paper continues our study on the adsorption and solution of weakly polar vapors with thin layers of water by means of gas-liquid chromatography. In particular we have examined the behavior of six new solutes: CH_2Cl_2 , CHCl_3 , CCl_4 , *cis* and *trans*-2-octene, and ethyl formate. Mixed mechanisms of retention were found for CH_2Cl_2 , CHCl_3 , CCl_4 and ethyl formate, the other solutes being retained solely by adsorption. In terms of partition, good agreement has been found for static partition coefficients and heats of solution with chromatographic data, lending further evidence to the similarity of the water coated in thin layers on wide-pore diameter silica with that of bulk water. In the case of the thermodynamic quantities of adsorption at zero coverage, it has been concluded that the adsorbed state can be considered as a gaseous or mobile film in most cases. Finally, the free energy and enthalpy of adsorption per methylene group has been found to be positive when methyl formate is compared with ethyl formate.

We have previously shown that gas-liquid chromatography can be used to study the thermodynamics of adsorption and partition of nonpolar or weakly polar solutes with thin layers of water coated on porous supports (1, 2). In the case of aliphatic hydrocarbons the mechanism of retention was solely one of adsorption, while for aromatic hydrocarbons, methyl formate, *n*-propyl ether, and several other weakly polar solutes both partition and adsorption simultaneously occurred. Contrary to the conclusions of other authors (3, 4), we found that at zero surface coverage the differential heats of adsorption for all the studied solutes in (1, 2) were less negative than the heats of liquefaction, except for *n*-propyl ether and methyl formate in which hydrogen bonding between the adsorbate and water surface was postulated to occur. This result indicated that the gas-liquid interface of water can be considered as a low energy surface, except for electron donating adsorbates. In the case

of partition, we found that the partition coefficient was independent of the amount of water coated on the solid support from a layer thickness of roughly 15 Å to several microns. In addition there were strong indications that the partition coefficients and heats of solution obtained at infinite dilution were the same as those obtained for bulk water using static measurements. In this paper we present further data relating to the above conclusions on adsorption and partition through an examination of the retention behavior of six new solutes.

EXPERIMENTAL

The apparatus and the details of the experimental procedure have been described elsewhere (1, 2). Porasil D (Waters Associates, Framingham, MA), specific surface area $\sim 29 \text{ m}^2 \text{ g}^{-1}$, was used as the solid support. The following solutes have been studied: methylene chloride (CH_2Cl_2), chloroform (CHCl_3), carbon tetrachloride

(CCl₄), *cis* and *trans* 2-octenes, and ethyl formate (Et-For). All compounds were reagent grade and were used as received. The first three compounds were obtained from J. T. Baker Chemical Co., *cis*-2-octene from Aldrich Chemical Co., *trans*-2-octene from Chemical Samples Co., and Et-For from Matheson Coleman and Bell.

The water used in these experiments was double-distilled in an all glass still. The column liquid loadings varied from 12–34% w/w. Enthalpies of adsorption and solution were obtained from the measurement of retention at five column temperatures from 5.7°–16.3°C. The temperature control was constant to $\pm 0.05^\circ\text{C}$.

THEORY

The theoretical basis of this work has been outlined previously (1). The general retention equation for solutes undergoing both partition and adsorption can be written as

$$V_N^0 = K_A A_L^0 + K_L V_L^0, \quad [1]$$

where V_N^0 = retention volume per gram of packing, K_A = adsorption coefficient, A_L^0 = interfacial surface area per gram of packing, K_L = partition coefficient, and V_L^0 = volume of water used as stationary phase per gram of packing. Using a gas-liquid interfacial area of 1.0 m²/g for a 20% water coated on Chromosorb P column (5), the adsorption coefficient for *n*-octane at 12.5°C was determined as 1.0×10^{-4} cm. Since *n*-octane has been shown to only undergo interfacial adsorption in its travel down the column (1), the interfacial surface areas per gram of packing for other columns can then be determined from the retention volume per gram of packing for octane (i.e., $A_L^0 = 10^4 V_N^0$). The adsorption coefficients for the components which are retained solely by adsorption can then be directly obtained. For solutes undergoing both partition and adsorption, K_A can be obtained from the least-squares determination of the slope of the straight line plot of V_N^0/V_L^0 vs. A_L^0/V_L^0 . The partition coefficient can then be obtained from the intercept of this plot. In order to check self-

consistency of Eq. [1], we also determined K_A and K_L from the straight line plot of V_N^0/A_L^0 vs. V_L^0/A_L^0 where K_A is now the intercept and K_L the slope. The values of K_A and K_L determined by both methods agreed within 2%. This agreement, along with the linear behavior of the plots, proves the validity of Eq. [1] for those solutes which are retained by interfacial adsorption and partition. As previously, virial coefficient corrections were negligible at the column temperatures and pressures.

RESULTS AND DISCUSSION

As we have already noted, the mechanism of retention of *n*-octane on columns of water coated on Porasil D is solely adsorption at the gas-liquid interface. Thus a study of the relative retention of the compounds in this work with respect to *n*-octane vs. the amount of water on the solid support can be a sensitive measure of mixed mechanisms of retention.

Table I presents the results for the relative retentions as a function of % H₂O. It can be seen that the relative retentions are independent of liquid loading for *cis* and *trans*-2-octene and it can be concluded that these two compounds are retained in the column solely (within the experimental limitations of our measurements $\pm 2\%$) by interfacial adsorption. On the other hand, one finds that the relative retention values for CH₂Cl₂, CHCl₃, CCl₄, and ethyl formate change with liquid loading. The increases in the relative retentions with % H₂O strongly suggest that partition and adsorption simultaneously occur for these compounds.

Influence of the Carrier Gas. Both helium and nitrogen were used as carrier gases under identical conditions in order to study the influence of this parameter on the gas chromatographic results. Apart from being diatomic, N₂ is more soluble and chemically more reactive than He. Moreover, inert gases are believed to increase the "structuring" in bulk water through the anomalously high partial molar heat capacity (6). However, no differences were found for the two gases in the retention volumes or differential

TABLE I
RELATIVE RETENTION WITH RESPECT TO *n*-OCTANE AS A FUNCTION OF % H₂O COATED ON
PORASIL D, T = 12.5°C

% H ₂ O (w/w)	Solute					
	CH ₂ Cl ₂	CHCl ₃	CCl ₄	<i>cis</i> -octene	<i>trans</i> -octene	Et-For.
12%	0.52	0.81	0.28	2.18	2.06	—
17%	0.63	0.88	0.29	2.16	2.05	1.04
23%	0.77	0.99	0.31	2.16	2.05	1.09
32%	1.43	1.44	0.37	2.15	2.03	1.38
34%	1.85	1.77	0.43	2.16	2.05	1.61

TABLE II
THERMODYNAMIC FUNCTIONS OF PARTITION OF VAPORS IN WATER AT 12.5°C

Solute	K_L		$-\Delta H_s^0$, kcal/mole		$-\Delta G_s^0$, kcal/mole		$-\Delta S_s^0$, e.u.
	Expt	Lit. ^a	Expt	Lit. ^a	Expt	Lit. ^a	
CH ₂ Cl ₂	19.2 ± 0.4	17.4	8.1 ± 0.1	7.8	1.68 ± 0.01	1.6	22.5 ± 0.5
CHCl ₃	13.8 ± 0.4	11.7	9.6 ± 0.3	9.7	1.49 ± 0.02	1.4	28.4 ± 0.8
CCl ₄	1.9 ± 0.1	1.6	9.8 ± 0.2	—	0.36 ± 0.03	0.3	33.0 ± 0.6
Et-For	9.0 ± 0.4	—	8.5 ± 0.1	—	1.25 ± 0.03	—	25.4 ± 0.1

^a Solubilities from A. Siedell, "Solubilities of Organic Compounds," Vol. II, 3rd edition, Van Nostrand, 1941; vapor pressures from R. R. Dreisbach, "Physical Properties of Chemical Compounds," Advances in Chemistry Series, #15, American Chemical Society, Washington, DC, 1955.

heats of adsorption in the case of solutes which are solely retained by interfacial adsorption. In the case of solutes with a mixed mechanism there seems to be a slight effect, particularly at the lower temperatures of operation. The retention volumes of these solutes with N₂ as the carrier gas were found to be as much as 7% lower in the case of CH₂Cl₂, CHCl₃ and CCl₄. This may be due to the differences in solubilities of the two gases in water. The retention volume differences decreased slowly as the temperature rose, until above 15°C there was no difference within experimental error, probably due to reduced solubility differences for the two gases. These results strengthen our previous interpretations (2) of the thermodynamic functions of distribution.

Partition. Using Eq. [1] and the calculated interfacial areas, as previously described, the partition coefficients for CH₂Cl₂, CHCl₃, CCl₄, and Et-For were determined as shown in Table II. Also included in this table are

the heats of solution ΔH_s^0 , the free energies of solution ΔG_s^0 , and the entropies of solution ΔS_s^0 , obtained in the standard manner. The experimental errors are included for each determined quantity.

The literature values of the heats and free energies of solution were obtained from the solubility of the components in bulk water (1, 2); however, the solubilities are sufficiently low that the approximation to infinite dilution is reasonable. It can be seen that the values determined in this work agree remarkably well with the literature values on bulk water. This agreement lends further weight to our previous arguments (2) that the water in thin layers coating the Porasil D support is close in properties to bulk water. This may be due to the fact that Porasil D is a wide-pore support, whereas most changes of water structure are found when the liquid is in very narrow pores (7). However, one must always exercise caution in

TABLE III
THERMODYNAMIC FUNCTIONS OF ADSORPTION OF VAPORS ON WATER AT 12.5°C

Solute	$K_A \times 10^{-4}$ cm	$-\Delta H_A^0$ kcal/mole	$-\Delta G_A^0$ kcal/mole	$-\Delta S_A^0$, e.u.	$-\Delta H_L^0$ kcal/mole
CH ₂ Cl ₂	0.39 ± .01	5.6 ± 0.1	3.67 ± .01	6.8 ± 0.3	6.8 ^a
CHCl ₃	0.71 ± .01	6.4 ± 0.1	4.01 ± .01	8.4 ± 0.2	7.3 ^a
CCl ₄	0.28 ± .01	5.6 ± 0.2	3.49 ± .01	7.4 ± 0.6	7.8 ^a
(CH ₂ Cl) ₂	1.70 ± .03	7.8 ± 0.2	4.51 ± .01	11.5 ± 0.5	8.5 ^a
cis-2-octene	2.16 ± .01	8.6 ± 0.1	4.65 ± .01	13.8 ± 0.3	9.8 ^b
trans-2-octene	2.04 ± .01	8.6 ± 0.1	4.61 ± .01	14.0 ± 0.3	9.8 ^b
Et-For	0.92 ± .01	6.9 ± 0.2	4.16 ± .01	9.6 ± 0.5	7.8 ^c
Me-For	4.7 ± 0.1	7.8 ± 0.2	5.09 ± .01	9.5 ± 0.5	6.2 ^a

^a J. D. Cop and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, NY, 1970.

^b R. R. Dreisbach, "Physical Properties of Chemical Compounds," Advances in Chemistry Series, #15, American Chemical Society, Washington, DC, 1955.

^c J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, NY, p. 408, 1950.

interpreting subtle behavior in terms of macroscopic properties such as solubility.

The activity coefficients at infinite dilution γ^∞ can be easily obtained from the experimental K_L values. For the first three solutes in Table II the γ^∞ values at 12.5°C are: CH₂Cl₂— 2.0×10^2 , CHCl₃— 6.4×10^2 , CCl₄— 9.2×10^3 , which is in the expected order (i.e., CCl₄ is the least soluble). The relatively large values of γ^∞ indicate that a substantial contribution of interfacial adsorption to the overall retention must exist (8), and this is what is found. Consistency with our previous results (2) is seen from the fact that γ^∞ for (CH₂Cl)₂ at 12.5° is 6.2×10^2 . For Et-For, γ^∞ is equal to 7.6×10^2 which is of the same order of magnitude as the other three solutes in Table II; however, for methyl formate we previously found γ^∞ to be 1.3×10^1 (2). This twentyfold difference in γ^∞ for the two esters is quite surprising. No explanation for this difference can be offered at this time.

Adsorption. The thermodynamic quantities for adsorption at zero coverage on the gas-liquid interface of water are shown in Table III. Also included for purposes of comparison are the corresponding data (2) for (CH₂Cl)₂, and methyl formate (Me-For). For K_A (and thus ΔG_A^0), the Kamball-Rideal Standard

State was chosen (9), and the liquid surface areas for the different columns were found as already noted. The experimental errors for each determined quantity are also included.

The heats of adsorption for all the solutes in Table III except Me-For were found to be less negative than the corresponding heats of liquefaction, ΔH_L^0 . This, in all probability, indicates that the adsorbed films in most cases are gaseous (or liquid-expanded) and mobile, the adsorbed films being held by relatively weak forces on the surface. More evidence for this conclusion will be presented shortly.

Jones *et al.* (10) studied the adsorption of CHCl₃ and CCl₄ at the gas-water interface using a static surface pressure measuring technique. The ΔG_A^0 and ΔH_A^0 values for both solutes at 15°C were found to be quite close to our values at 12.5°C [e.g., $\Delta G_{\text{CHCl}_3}^0 = -3.8$ kcal/mole, $\Delta G_{\text{CCl}_4}^0 = -3.3$ kcal/mole; $\Delta H_{\text{CHCl}_3}^0 = -7.3$ kcal/mole, $\Delta H_{\text{CCl}_4}^0 = -6.0$ kcal/mole; c.f. values in Table III]. They also calculated the theoretical translational entropy change (ΔS_{trans}) due to adsorption using the Sackur-Tetrode equation and the Kamball expression (11) for the two-dimensional translational entropy for a surface molecule. The ΔS_{trans} for CHCl₃ and CCl₄ were calculated to be, respectively, -9.3 and -9.6 e.u. at 15°C, which compares

favorably to our experimental ΔS_A^0 's of -8.0 and -7.0 e.u. at 12.5°C , respectively. Such agreement strongly points to the loss of only one degree of translational freedom upon adsorption and to a mobile film on the surface.

A comparison of CH_2Cl_2 , CHCl_3 , and CCl_4 indicates some interesting behavior. While the heats of liquefaction increase uniformly by -0.5 kcal/mole for each additional chlorine, chloroform has the highest negative values of ΔH_A^0 and ΔG_A^0 . It appears that CCl_4 is somewhat anomalous, and its low values of ΔH_A^0 and ΔG_A^0 may be related to the fact that the molecule possesses no permanent dipole for dipole orientation interactions with the water surface. It is further noted that $(\text{CH}_2\text{Cl})_2$ has a substantially larger $-\Delta H_A^0$ than the other three chlorine-containing compounds. Undoubtedly the two C-Cl dipoles in the molecules are sufficiently far removed that they do not completely cancel each other. It is expected that some dipole orientation interaction will occur for both dipoles in the adsorption process. In addition the increase in entropy of -5 e.u. for $(\text{CH}_2\text{Cl})_2$ over the other three adsorbates is indicative of the loss of some rotational entropy, probably caused by the anchoring of one or both chlorines to the surface, with the $-\text{CH}_2\text{-CH}_2$ -chain lying above the surface. Theoretical calculation using the method of Kemball (11) showed an entropy decrease of -6.3 e.u. per degree loss of freedom of rotation, in this case. This could be due to the restricted rotation of one of the ClCH_2 -groups as a result of adsorption. In the case of adsorbates such as CH_2Cl_2 , however, the molecules would be expected to be far more labile.

Both *cis* and *trans*-2-octene show strong adsorption, with the thermodynamic functions being similar for both isomers within experimental error. These results indicate that both *cis* and *trans*-2-octene are similarly oriented at the gas-liquid interface. Using the same calculation procedure as Jones

et al. (10) for the translational entropy change upon adsorption, we again find a value for ΔS_A^0 of -9 e.u. if one translational degree of freedom is lost. The experimental value for ΔS_A^0 is -14 e.u. for both isomers which may indicate some rotational loss of entropy by the proximity of the double bond to the water surface. The difference, -5 e.u., compares remarkably well with the value of -5.1 e.u. estimated being due to restricted rotation of one of the carbon atoms in straight chain hydrocarbons (11), presumably a methyl group close to the double bond and to the surface.

Finally, it is of interest to compare Me-For and Et-For. We have previously shown (2) in the case of homologous *n*-alkane series that per methylene group, ΔG_A^0 increased by -0.5 kcal/mole and ΔH_A^0 increased by -1.0 kcal/mole. However, the changes in ΔG_A^0 and ΔH_A^0 are both $+0.9$ kcal/mole from Me-For to Et-For. While this result is surprising, it must mean that the ester linkage can interact more favorably with the water surface in the case of Me-For. The reasons for this behavior are unclear at the present time. However, it is worth noting that Corkill *et al.* (12) also observed similar positive free energy and heat changes per methylene group in the case of micellization of *n*-alkylsulfanylalkanols in water. They noted this behavior for the $-\text{CH}_2$ -groups in between the sulfoxide and the hydroxyl groups as opposed to those remote from the polar group.

A study of the adsorption isotherms of a series of hydrocarbons solutes that do not partition under the conditions of these experiments has recently been completed in our laboratory. In the near future we shall report on these results including an examination of the isosteric heats of adsorption as a function of surface coverage and equations of state for the adsorbed species.

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REFERENCES

1. KARGER, B. L., SEWELL, P. A., CASTELLS, R. C., AND HARTKOPF, A., *J. Colloid Interface Sci.* **35**, 328 (1971).
2. KARGER, B. L., CASTELLS, R. C., SEWELL, P. A., AND HARTKOPF, A., *J. Phys. Chem.* (in press).
3. HAUXWELL, F., AND OTTEWILL, R. H., *J. Colloid Interface Sci.* **28**, 514 (1968).
4. ADAMSON, A. W., DORMANT, L. M., AND OREM, M. W., *J. Colloid Interface Sci.* **25**, 206 (1967).
5. MARTIRE, D. E., PECSOK, R. C., AND PURNELL, J. H., *Trans. Faraday Soc.* **61**, 2496 (1965).
6. BEN-NAIM, A., *Trans. Faraday Soc.* **66**, 2749 (1970).
7. RESING, H. A., *Advan. Mol. Relaxation Processes* **1**, 109 (1968).
8. MARTIRE, D. E., *Anal. Chem.* **38**, 244 (1966).
9. KEMBALL, C., AND RIDEAL, E. K., *Proc. Roy. Soc. A* **187**, 53 (1946).
10. JONES, D. C., OTTEWILL, R. H., AND CHATER, A. P. J., 2nd International Congress on Surface Activity, London, 1957, p. 188.
11. KEMBALL, C., *Proc. Roy. Soc. A* **187**, 73 (1946).
12. CORKILL, J. M., GOODMAN, J. F., AND TATE, J. R., in "Hydrogen-Bonded Solvent Systems" (A. K. Covington and P. Jones, Eds.), Taylor & Francis Ltd., London, p. 191, (1968).